

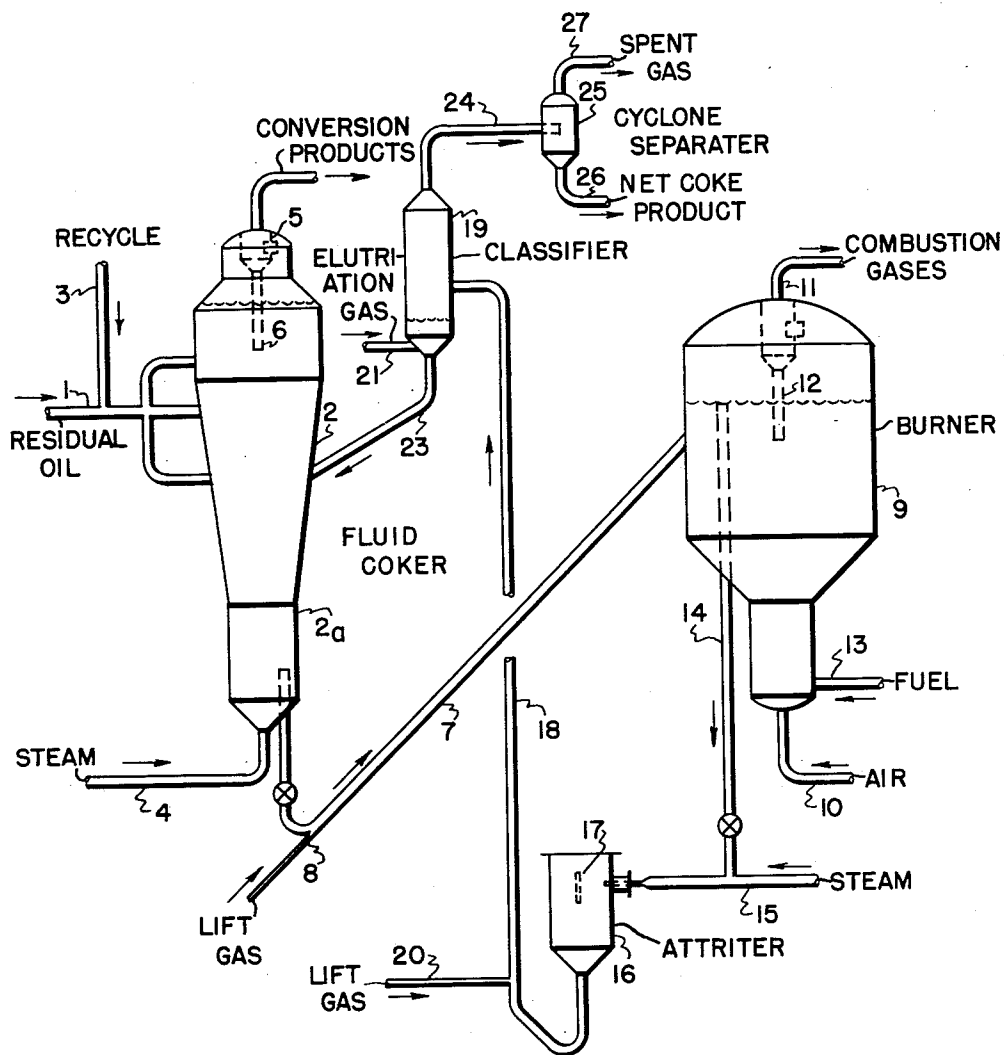
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SEED COKE PRODUCTION IN FLUID COKING SYSTEMS

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This invention pertains to a process for treating hydrocarbons, and more particularly relates to the coking of heavy residual oils in a fluidized solids process to produce lower boiling hydrocarbons and coke. More particularly, the present invention pertains to an improved hydrocarbon oil fluid coking process wherein the requisite seed coke or growth nuclei are created by means integral with the process, and wherein a net coke product of boiler fuel size is produced.

The hydrocarbon oil which is to be coked according to the present process is preferably a high boiling hydrocarbon oil which cannot be vaporized at ordinary pressures without cracking the high boiling constituents. The residual oil may be that produced by distilling crude petroleum oil at ordinary atmospheric pressure or under subatmospheric pressure such as by vacuum distillation. Broadly, however, the present process may also be used for pyrolytically upgrading or coking charging stocks comprising shale oils, pitches, tars, coal tars, asphalts, cycle stocks, extracts, synthetic oils, whole crudes, distillate or residual fractions therefrom, or mixtures thereof.

Processes are known in the prior art for cracking or coking residual oils in the presence of finely divided catalytically inert, or substantially catalytically inert, high temperature solids maintained as a fluidized bed.

In the present process a dense fluidized bed of finely divided catalytically inert refractory solids such as sand, metal beads, spent catalyst, etc., but especially particulate coke produced by the process, is used and the preheated residual oil is introduced into the dense fluidized bed of the finely divided solids maintained at a coking temperature. Vaporous products of coking are taken overhead and further treated as desired to recover lower boiling hydrocarbon fractions. During the coking, more coke is formed than is required to be burnt to supply heat to the process and a net coke product is withdrawn from the process. Coke particles from the coking zone or reactor are stripped to remove volatile hydrocarbons therefrom and are passed to a burner wherein they are preferably maintained in a dense fluidized condition and contacted with air or other free oxygen-containing gases to burn some of the coke particles and to reheat the coke particles. The heated coke particles at a temperature of 50° to 400° F. above the coking temperature are then comminuted by jet attrition and the comminuted material is then classified to obtain a relative coarse fraction which is returned to the coking zone to supply heat and growth nuclei. The net coke product of the process is obtained from the comminuted material and comprises the relatively fine coke separated by the classification. The attrition of the coke is sufficient to meet the seed coke requirement of the process besides creating a finely divided coke product.

One of the problems in the fluid coking of residual or other heavy oil feeds is the control of the particle size of the coke particles in the circulating coke stream. The most desirable particle size range for circulation in the system is that from about 40 to 400 microns, although some of it may be of a size up to 1000 microns or so. There is a gradual increase in size of the particles being circulated because more coke is produced than is required to be burnt to supply heat. The coke made from the oil feed is deposited on the particles regardless of size

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and in a substantially uniform layer. As the circulating coke particles become coarser, fluidization becomes poor, circulation more erratic and contacting efficiency decreases.

As the weight rate of coke combustion is a function primarily of surface area, the above condition of particle size accretion is aggravated by the combustion step in the burner because the smaller coke particles, weight for weight, have a relatively larger surface than the larger particles and will therefore be preferentially burnt by the free oxygen-containing gas in the burner.

It has been found that the amount of coke produced by a fluid coking system is related to the Conradson carbon of the feed. For feed stocks ranging from about 5 to 30 wt. percent Conradson carbon, e.g., 20 wt. percent, about 6 to 33 wt. percent, e.g., 22% based on feed of coke will be produced and from 0 to 100% of this will be burnt to supply heat, the remainder being withdrawn as product. This coke product will usually amount to about 5 to 30 wt. percent, based on feed. Of the coke circulating in the system, about 0.05 to 0.5 lbs./lb. of feed, e.g., 0.2 lb./lb., has to be reduced in size in some manner to form seed coke in order to maintain the size and size distribution of the coke particles in the system substantially constant.

Previous coking processes in order to maintain the weight inventory, numerical inventory and size distribution of the particulate coke constant have proposed withdrawing coarse coke particles from the unit, grinding them and returning the ground particles to the unit as seed coke or growth nuclei.

In the past, it has been found desirable to utilize the product coke produced in a fluid coking system as fuel for conventional powdered coal boilers and the like. It is necessary, however, to grind or otherwise reduce in size the coke to a particle size much smaller than that normally used in the coking system. To be suitable for use as a fuel, the coke should be about 200 mesh (74 microns) or smaller. Most previous processes have proposed that this grinding be accomplished by means essentially separate from the coking system. In the past, if jet attrition grinding has been used to obtain this boiler fuel, some means of pressurizing the coke stream, e.g., as by standpipes, has been necessary. High pressure drops are required in jet attrition grinding systems because very high velocities in the jet are required in order to obtain high conversions of the fluid coke to minus 200 mesh material.

It is a prime object of the present invention to present to the art an improved hydrocarbon oil fluid coking process. A more particular object is to devise a means for comminuting fluid coke that is integrated with the fluid coking system, whereby a net coke product of the coking process may be withdrawn that is suitable for use as a boiler fuel. Another object is to devise a jet attrition grinding scheme for use in the fluid coking process that makes efficient use of the natural pressure drops in the system whereby the seed coke requirements in the process are met and a finely divided net coke product is obtained.

Other objects and advantages of this invention will appear as this description proceeds during which the attached drawing, forming a part of the specification, is described in detail. The drawing depicts one form of apparatus and mode of operation thereof adapted for carrying out the present invention, but this showing is for the purpose of illustration only and the invention is not to be restricted thereto.

According to the present invention, a jet attrition system for the size reduction of the fluid coke is incorporated within the coke circulation system of a fluid coking process. Preferably this attrition is carried out on the reheated

coke circulated from the heating vessel to the coking vessel. The comminuted product of the jet attriter is then classified, preferably by elutriation, and the coarser material, which comprises a major part of the attriter product, is then circulated to the coker to supply heat thereto. The finer fractions of the coke separated in the elutriator are withdrawn from the process as net coke product. By operating in this manner, the required conversion per pass of the size reduction system is quite low. Thus low velocities can be employed in a jet attriter and consequently the low pressure drops required by the attriter are well within those which can be obtained in the coking circulating system. As an example, a typical coking process may operate at a 10/1 solids/oil ratio and produce 20% net coke on feed. In this case, the required conversion per pass in the process of this invention is only 2%. This 2% conversion per pass can be readily obtained at gas velocities of about 300 ft./sec. with a total pressure drop of less than 10 p.s.i.

By suitable design, this invention utilizes the attrition gas to elutriate the comminuted coke which results in a considerable saving.

In brief compass, this invention proposed an improved hydrocarbon oil fluid coking process which comprises injecting an oil into a coking zone containing fluidized particulate coke maintained at a coking temperature to form relatively lighter hydrocarbon vapors and a coke or carbonaceous residue which is deposited on the coke particles, causing them to grow in size, removing the vapors overhead as product, circulating stripped coke particles from the lower portion of the coking zone to a heating zone wherein they are heated to a temperature 50° to 400° F. above the coking temperature, comminuting the reheated coke particles by impelling the particles by means of a high velocity fluid stream against an impact surface, elutriating the comminuted particles to separate relatively fine particles, passing the remaining comminuted particles to the coking zone to supply heat and growth nuclei thereto, and removing the relatively fine particles from the process as net coke product.

With particular reference to the attached drawing, a preferred coking process incorporating the teachings of this invention will be described. A heavy oil which may be suitably preheated, is injected into a coker 2 via line 1. Recycled heavy ends separated from the coker effluent may be incorporated with this injected oil by line 3. The oil feed comprises, preferably, a residual petroleum oil such as a top crude or vacuum residua having an API gravity between about -5 and 20°, a Conradson carbon between about 5 and 50 wt. percent and an initial boiling point between about 850° and 1200° F. The coking zone 2 contains a fluidized bed of finely divided inert particles, preferably particulate coke. The dense bed has a definite upper level with a dilute or disperse phase thereabove. The inert solids of the fluidized bed have a particle size between about 20 and 800 microns, preferably between about 40 and 400 microns. The fluidized bed is maintained at a temperature between 850° and 1600° F., preferably between about 900° and 1100° F.

The fluidized bed is maintained as such by the upflowing hydrocarbon gases and vapors formed by the coking of the oil feed and by the steam added to the process via line 4. The superficial velocity of the gases and vapors passing upwardly through the bed is between about 0.5 and 4 ft. per second. When using finely divided coke of about 40 to 400 microns and at a superficial velocity of about 1 to 2 feet per second, the density of the fluidized bed will be about 35 lbs. per cu. ft. but may vary between about 15 and 60 lbs. per cu. ft. depending on the gas velocity selected and the particular particle size range.

Vaporous products of coking leave the bed and pass overhead through cyclone separator system 5 arranged at the top interior of the reactor 2. The vaporous reaction products leaving the coking zone contain entrained

solids and the cyclone separator 5 or other gas-solids separating device is used to separate or recover the entrained solids and return them to the dense fluidized bed through dipleg 6. More than one cyclone separator in stages may be used and the cyclone separator or separators may be arranged externally of the reactor 2.

The coker products may, of course, be subjected to further conventional processing. For example, the gas oils may be catalytically cracked and the naphtha hydrodesulfurized. The heavy ends of the vapors boiling above about 950° F.-1050° F., which will contain catalyst contaminants and refractory constituents can be recycled via line 3 to the coker for further treatment.

Coke particles are withdrawn downwardly from the dense bed into stripping zone or vessel 2a which is shown as having a smaller diameter than reactor 2 and which extends down from reactor 2 as an integral structure. Other forms of strippers may be used. Steam or other stripping gas is introduced through line or lines 4 into the bottom portion of the stripping zone 3 to remove volatile hydrocarbons from the coke in the stripping zone and then passed upwardly into the dense fluidized bed in the reactor 1. The temperature in the stripping zone is between about 800° and 1600° F. and the velocity of the upflowing gas in the stripper may be between about 0.4 and 3.0 feet per second to maintain a dense fluidized mixture. Baffles may be placed in the stripping zone to increase the contact efficiency.

Stripped coke particles are removed from the bottom of the stripper and circulated to a burner 9 through line 7 to which conveying or lift gas is added through one or more lines 8. The standpipe and riser conveying system used to transport the solids is conventional, and is known by the art.

Air or other free oxygen-containing gas is admitted to the base of the burner by line 10 and serves to fluidize and burn the particles. The temperature of the burner may vary from about 1000° to 2000° F. Combustion gases are withdrawn overhead by line 11 after having entrained solids removed by cyclone system 12. In cases where it is desired to maximize the amount of coke produced by the process, lesser value fuels may be preferentially burnt in the burner, e.g., light gases or residual oils may be admitted to the burner by line 13.

As will be apparent to those skilled in the art, other means of supplying heat to the process may conveniently be used. Thus, a transfer line burner, gravitating burner, shot heating system, or other direct or indirect heating means may be used.

The reheated coke at a temperature of 50° to 400° F. above the coking temperature overflows into standpipe 14. At the base of the standpipe, the reheated particles are engaged by high velocity fluid medium, e.g., steam, supplied by line 15. This high velocity gas serves to accelerate the particles in line 15 to solid velocities in the range of 50 to 1000 ft./sec. The high velocity particles are then directed into an attriter 16 wherein they impact a fixed target 17. This impacting shatters and reduces in size the coke particles. The comminuted particles along with the spent acceleration gas then flow downwardly out of the attriter 16 through line 18 and are conveyed to an elutriator 19. Conveying or lift gas may be admitted to line 18 by line 20 to help convey the particles.

In the elutriator, the coarser particles fall into the base of the vessel and the finer particles are conveyed by the lift gas and spent acceleration gas upwardly through the elutriator. Additional gas, e.g., steam, can be admitted by line 21 to the base of the elutriator to achieve the desired velocities therein. It will be usually desired to remove overhead from the elutriator particles having a size smaller than about 50 to 100 microns, e.g., 75 microns. Consequently, gas velocities in the range of about 1 to 20 ft./sec., e.g., 5 ft./sec., will be used in the elutriator. Approximately .05 to 5%, e.g.,

2% of the coke circulated to the elutriator will be removed overhead from the elutriator. The remaining relatively coarse material at the base of the elutriator is circulated to the coking vessel 2 by line 23 to supply heat and seed coke thereto. As will be appreciated, by this placement of the elutriator, the conveying gas used to circulate the coke and the acceleration gas do not enter the coker and do not therefore, dilute the coker products.

The finer portions of the coke and spent gas are conveyed by line 24 to a solids separator system, e.g., a cyclone system 25. Net coke product of the process is removed from the cyclone by line 26 and the spent gases are discharged overhead by line 27.

It is preferred to place the elutriator and attriter as shown. That is, the attriter is at an elevation below the fluid bed of the burner and the elutriator at an elevation above the fluid bed in the coker. By this placement, maximum use is made of the available pressure drop in the coker system. The positions of these vessels may be varied, however, as is desired. Further, although it is preferred to attrite the reheated coke as it is more friable than the spent coke from the coker, this invention is inclusive of attriting the coke circulated from the coker to the burner.

For convenience, the range of pertinent operating conditions applicable to this invention are summarized in Table I. This table also presents a specific example of operating conditions.

Table I

	Range	Example
Coker and Burner:		
Coking temperature, °F.....	850-1,600	950
Pressure @ coker outlet, p.s.i.g.....	0-400	6
Feed rate, w/w/hr.....	0.2-2.0	0.5
Burner temperature, °F.....	1,000-2,000	1,125
Coke Circulation rate, lbs./lb feed.....	5-20	10
Superficial fluidization gas rate, f./s.....	0.2-5	3
Percent 1,050 ° F. conversion ¹	70-100	100
Attriter:		
Solids loading, lbs./cu. ft.....	0.2 to 5	0.6
Maximum solids velocity, f./s.....	200 to 2,000	300
Conversion to minus 200 mesh/pass.....	1 to 5	1.7
Pressure drop, p.s.i.....	5 to 20	10
Mass velocity, lbs./ft. ² /min.....	3,000 to 30,000	11,000
Classifier (elutriator):		
Classification gas velocity, f./s.....	1 to 20	5
Solids loading, lbs./cu. ft.....	0.2 to 5	0.6
Maximum coke product size, microns.....	50 to 200	100
Percent of attrited coke returned to coker.....	90 to 99+	98
Wt. percent of coke product, based on feed.....	5 to 30	20

¹ 1,050 ° F. conversion is defined as: 100 vol. percent feed—vol. percent product boiling above 1050° F., based on fresh feed, excluding coke.

Table II presents the products obtainable by the process of this invention as depicted in the drawing when operated in accordance with the example of Table I. Table III lists the size distribution of the various coke streams.

Table II

Feed: 30-40% Hawkins residuum.	
H/C atomic ratio.....	1.5
Gravity, ° API.....	8
Conradson carbon, wt. percent.....	20
Ash @ 800° C., wt. percent.....	0.1
Products: percent based on feed.	
C ₃ -gas, wt. percent.....	9
C ₄ /430° F., vol. percent.....	23.5
430°/1050° F., vol. percent.....	56
Gross coke make, wt. percent.....	22
Net coke product, wt. percent.....	17

NOTE.—All 1050° F. material is recycled to extinction.

Table III

Wt. percent smaller than—	Circulating coke	Attriter product	Net product
800 microns.....	98	99	98
400 microns.....	90	91	90
295 microns.....	70	72	71
246 microns.....	50	53	52
175 microns.....	20	23	22
147 microns.....	10	13	12
74 microns.....	0	1.7	0
20 microns.....	0		

In jet attrition of fluid coke to produce coke of seed size and/or of boiler fuel size, the rate of production of the finer material increases as the gas velocity increases. However, as gas velocity increases, fluid wall friction increases (in proportion to the square of the velocity) and, consequently, the pressure drop and non-useful power consumption increases sharply. In a commercial fluid coking system, there exists a certain constant and maximum amount of pressure drop which is available for attrition purposes. There is then, in a commercial system, an optimum gas velocity to be used in a jet attriter apparatus, corresponding to the available pressure drop, which will secure a maximum reduction in size of the coke particles. To define this optimum, it has been found that the production of particles smaller than a certain size, e.g., 100 mesh, per unit of time (R) can be represented by the following equation:

$$R = cA \frac{p}{T} (p - kV^m)^s$$

where:

- k, c, and s are constant for a particular apparatus.
 m is a constant essentially equal to 2.
 A is the cross-sectional area of the acceleration tube at the outlet.
 V is the outlet gas velocity.
 P is the pressure drop available.
 p is the operating pressure.
 T is the operating temperature.

For a given case, all values of this equation are constant except R and V. To determine the optimum velocity, this equation is differentiated, the derivative equated to zero and the resulting equation solved for V. Thus:

$$V_{\text{optimum}} = \left(\frac{P}{k(2s+1)} \right)^{\frac{1}{m}}$$

- All the terms of the second equation are constant for a given installation, and the constants may be determined from a single test or from correlations. The following Table IV illustrates the range of values the terms of the equations may have and presents a specific example.

Table IV

	Range	Example
Available pressure drop, P, p.s.i.....	5 to 60	8
Optimum gas velocity, V optimum.....	300 to 2,000	495
Solids loading, lbs./c.f.....	0.01 to 10	0.15
Tube length, ft.....	1 to 6	1
Tube size.....	1/4 to 8"	0.25"
Cross-sectional area, A, in. ²	0.049 to 50	0.43
K.....	1 × 10 ⁻⁶ to 1 × 10 ⁻⁴	1.25 × 10 ⁻³
s.....	0.5 to 1.0	0.8
m.....	Essentially 2	2.0

The effect of operating at other velocities, other than optimum is shown by Table V. This table compares the production of material finer than 147 microns (seed coke) as a function of attriter velocity. The total available pressure drop, P, was 8 p.s.i. The coke feed to the attriter had a size in the range of 74 to 800 microns, with 250 microns being the median particle size. The acceleration tube was 6 ft. long, and 0.43" in cross-section.

tional area, and was spaced 2 inches from a flat target surface.

Table V

Solids Loading, Lbs./s.c.f.	Tube Outlet Gas Velocity, ft./sec.	147 microns product, lbs./dy.
0.37	300	1,700
0.20	400	2,030
0.11	500	2,160
0.05	600	1,980

Table V clearly illustrates the effect of gas velocity on maximum production of fines at a constant pressure drop. The optimum velocity, 500 ft./sec., compares favorably to that calculated by the above equation, i.e., 495 ft./sec.

In summary, it can be seen that this invention provides for a method of jet attriting all the coke circulated between the coking vessel and the heating vessel of a fluid coking system whereby the seed coke requirements of the system are satisfied and a finely divided net coke product is obtained. By attriting all of the circulating coke, only a small conversion per pass is required of the attriter. Various modifications and other alternative modes of operation of this invention will be apparent to those skilled in the art. Having described the invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. An improved hydrocarbon oil fluid coking process, comprising injecting a charging stock into a coking zone containing fluidized particulate coke having a size substantially in the range of 40 to 800 microns maintained at a coking temperature to form relatively lighter hydrocarbon vapors and coke which is deposited on said particulate coke causing the particles to grow in size, removing said vapors as product, circulating stripped coke particles from the lower portion of said coking zone to a heating zone wherein the particles are heated to a temperature 50° to 400° F. above said coking temperature, comminuting the reheated coke particles at a conversion to minus 74 micron material per pass in the range of 1 to 5% by impelling all of the particles withdrawn from

the heating zone without substantial cooling by means of a high velocity gas stream against an impact surface, elutriating the still hot comminuted particles utilizing the impelling gas to separate relatively fine minus 74 micron particles, passing the remaining hot comminuted particles to said coking zone to supply heat and growth nuclei thereto, and removing said relatively fine particles from said process as net coke product in an amount of from 5 to 30 wt. percent of the hydrocarbon oil charging stock.

2. An improved method for comminuting fluid coke in a two vessel hydrocarbon oil fluid coking system wherein a charging stock is converted in a coking zone by contact with high temperature fluidized coke particles having a size substantially in the range of 40 to 800 microns, and wherein said coke particles are continuously circulated to an external heating zone and back via a standpipe and riser system to maintain the conversion temperature which comprises accelerating all of the reheated coke particles withdrawn from the heating zone without their being substantially cooled by means of a high velocity fluid medium and impacting all of the still hot particles against an impact surface at a conversion to minus 74 micron material per pass in the range of 1 to 5%, utilizing the pressure head created by the standpipe for returning the reheated coke particles to said coking zone, upwardly conveying the impacted hot particles to an elutriation zone substantially above said coking zone, and classifying the impacted material therein to obtain a minor amount of relatively fine minus 74 micron material, returning the remaining hot material to the coking zone to supply requisite thermal energy thereto, and withdrawing the relatively fine material as product in an amount of from 5 to 30 wt. percent of the charging stock.

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